# Novel Materials from Solgel Chemistry


Crayons on top of an aerogel are protected from the flame below. (Reprinted courtesy of NASA and Jet Propulsion Laboratory, California Institute of Technology.)

SOLGEL chemistry is a remarkably versatile approach for fabricating materials. Scientists have used it to produce the world's lightest materials and some of its toughest ceramics. Chemists in Livermore's Advanced Materials Synthesis (AMS) Group are working to improve the solgel process so they can specify the properties in the materials they are designing.

In solgel chemistry, nanometer-sized particles form and then connect with one another to create a three-dimensional (3D) solid network. This technique allows scientists to change the composition and structure of materials on the nanometer (billionth-of-a-meter) scale. In addition, this process can be modified to produce solgel materials in different forms, such as powders, films, fibers, and freestanding pieces of material called monoliths. For example, a gel can be dried in a solgel process to make aerogels, a special class of ultralow-density materials. In fact, the Livermore group created an aerogel weighing only 1.0 milligram per cubic centimeter, which is listed in the *Guinness Book of World Records 2005* as the lightest material on Earth.

But the AMS chemists do much more than create aerogels. With solgel chemistry, they can create a broad set of materials for applications such as optics coating, waste remediation, energy storage, ceramics, and nanoelectronics. To optimize the fabrication process for new materials, they are also developing a methodology to selectively control the physical properties of the resulting materials. Once it is refined, this capability will revolutionize the way these materials are prepared.

## A Mastery of Solgel Chemistry

In the solgel process, simple molecular precursors are converted into nanometer-sized particles to form a colloidal suspension, or sol. The colloidal nanoparticles are then linked with one another in a 3D, liquid-filled solid network. This transformation to a gel can be initiated in several ways, but the most convenient approach is to change the pH of the reaction solution. Even the method used to remove liquid from a solid will affect the solgel's properties. For example, to preserve a gel's original 3D structure and produce low-density aerogels, chemists use a technique called supercritical drying. If, instead, the gel is dried slowly in a fluid-evaporation process, the gel's structural network collapses, which creates a high-density material known as a xerogel. (See *S&TR,* October 2000, pp. 19–21.)

Alkoxides—compounds formed by the reaction of an alcohol and an alkali metal—are a common precursor in solgel chemistry. However, alkoxides can be very reactive and are commercially available for only a select number of elements, which limits the types of materials that can be prepared. In studying the mechanisms that drive the solgel process, the Livermore chemists found that organic epoxides would also initiate the reaction. With this approach, precursors that are more widely available can be used, thus increasing the number of potential materials that can be developed. In addition, the starting materials, solvents, and gelling agents used with epoxides are less expensive than those used with alkoxides. Reducing the production costs may increase commercial interest in the new solgel materials.

"That's the beauty of working with epoxides," says Livermore chemist Joe Satcher, who leads the AMS Group. "We can use readily available starting materials and simple benchtop chemistry techniques. Right now, we're making new materials in a beaker, but this process is readily scalable."

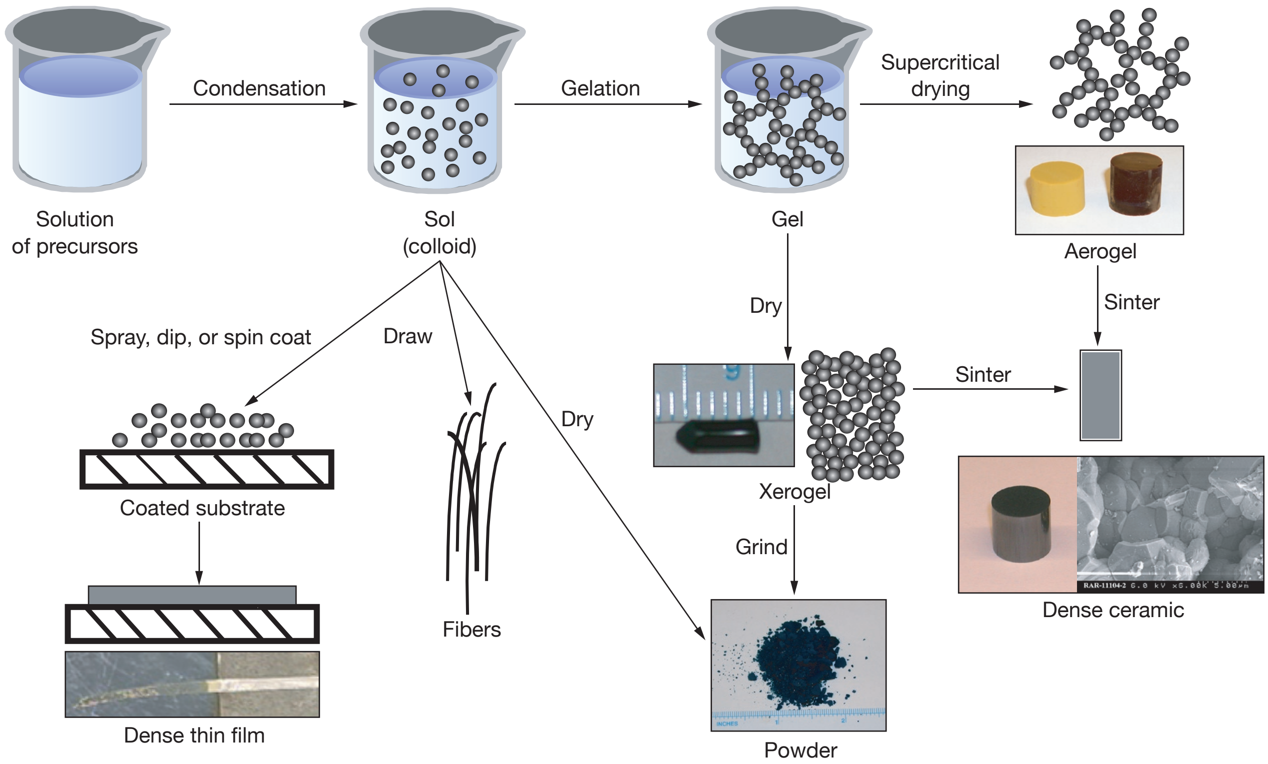
Because the group's solgel process is so flexible, the chemists have been systematically going through the elements in the periodic table, creating materials composed of different metal oxides or of organic and inorganic elements. For example, they have developed solgels that are organic networks with an inorganic component and others that are inorganic networks with an organic component.

As a result of this systematic effort, the AMS Group has created a broad range of materials. For example, one composite has been designed to remove oil from water. This porous material is hydrophobic—it repels water—but absorbs organics such as oil. A similar aerogel composite is used to remove contaminants such as uranium, chromium, and arsenic from groundwater. The group also has developed an energetic composite—a material that stores energy chemically—by mixing an oxidizer and a fuel at the nanometer scale. The result is an energetic material that provides both high energy density and high power; that is, it will release an enormous amount of energy very quickly. Other new solgel materials include ultrathin films, which can be used to coat silicon wafers and protect optics, and solgel-derived powders, which can be used to produce ceramics with various properties.

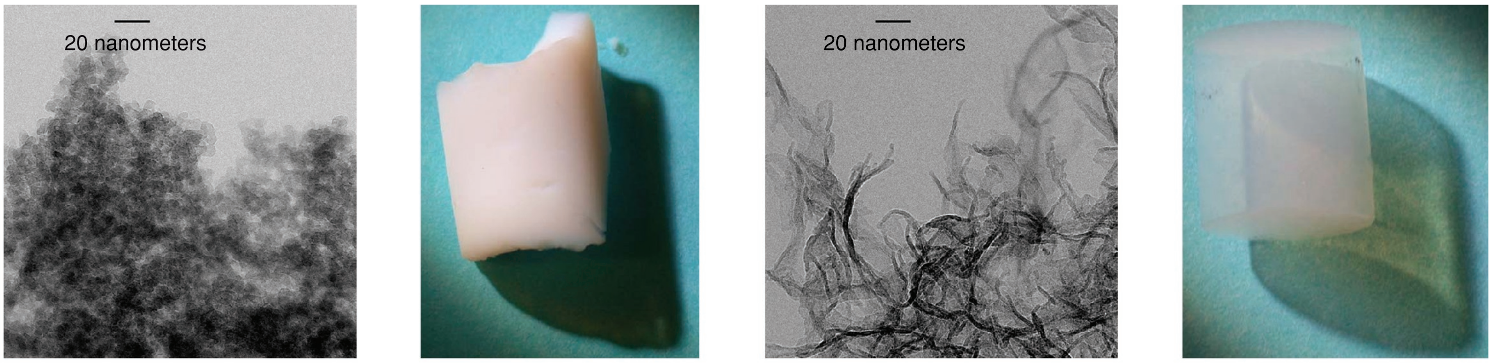
The Livermore group is also working on a project in support of the Department of Energy's (DOE's) Centers of Excellence for exploratory research in hydrogen storage. This DOE effort is addressing a major technical barrier for hydrogen-powered vehicles, which is to store enough hydrogen on board so a vehicle can travel more than 300 miles without refueling and without reducing the cargo or passenger space. For this project, the AMS chemists are experimenting with a metal–carbon aerogel composite that can store, transport, and release hydrogen at reasonable operating temperatures and pressures.

## Observing the Process in Action

According to Satcher, the next goal for the AMS chemists is to better understand the subtleties of their new method. For example, they want to determine what happens when different precursors or solvents are used in the colloidal solution and gelation stages and how different methods for extracting liquids will affect the drying stage. To meet this goal, they are examining the mechanisms by




In solgel chemistry, molecular precursors are converted to nanometer-sized particles, to form a colloidal suspension, or sol. Adding epoxide to the sol produces a gel network. The gel can be processed by various drying methods (shown by the arrows) to develop materials with distinct properties.




Aerogel properties can be changed by adding different precursor molecules. For example, (a) an aluminum oxide foam prepared from aluminum nitrate has a cluster morphology that results in (b) an opaque aerogel. (c) Using aluminum chloride as the precursor produces an aerogel with fibrous morphology, resulting in (d) a stronger foam that is also translucent.

which the molecules form, aggregate, and assemble and how these processes influence the physical properties of the solgel materials.

For these experiments, the Livermore group is using nuclear magnetic resonance (NMR) spectroscopy to view the process as it happens, from sol formation to gelation to processing the composite material. NMR is ideal for this task. This nondestructive technique can be used to selectively track changes in the solution, gel, and solid phases. Details from the NMR experiments will help the chemists understand the relationship between the synthetic variables introduced in the process and the physical properties of the final material.

For example, in one experiment, the group is using NMR spectroscopy to monitor structure formation in two types of aluminum oxide aerogels. (See the figure above.) Changing a single variable—the precursor molecule—in the solgel reaction generates two different aerogels. Although the aerogels are composed of the same material, their morphologies—that is, their form and structure—and their mechanical properties are dramatically different. When the precursor is aluminum nitrate, the aluminum oxide foam has a random cluster morphology, and the resulting aerogel is opaque. Using aluminum chloride as the precursor produces an aerogel with fibrous morphology, which creates a stronger foam that is also translucent.

### Solgel Materials of the Future

The AMS Group is expanding the number of materials that can be produced with the improved method. With each new material created, the group learns more about controlling the variables in the process. "Our goal is to replace chemical intuition with a systematic approach, so we can prepare a particular composition with well-defined chemical and physical properties," says Satcher. "We've demonstrated this capability for some compositions, but we want to understand the solgel process so well that we can determine a material's properties before we even start."

By working methodically through the periodic table and using techniques such as NMR spectroscopy, the AMS Group is closer to achieving this goal.

*—Karen Rath*

**Key Words:** aerogel, gelation, polymerization, solgel chemistry, supercritical drying, xerogel.

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